

## PYROLYSIS OF SHALE OIL RESIDUAL FRACTIONS

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### INTRODUCTION

JP-5, the Navy jet fuel, must meet many stringent requirements if satisfactory performance in aircraft and fuel handling and storage systems is to be attained (1). In considering JP-5 derived from alternate fossil fuels, several properties are affected more by the chemical characteristics of the fuel than by the physical properties. The important specification requirements may be primarily controlled by elemental composition, the amounts of each of the hydrocarbon classes - paraffin, naphthene, aromatic, olefin - or by specific chemical compounds. The three critical properties which are controlled by composition are (a) low temperature properties, (b) fuel stability, and (c) combustion behavior.

Low temperature properties of concern are fuel freezing point and viscosity. The freezing point is the property of concern in this paper. Jet aircraft are exposed to low temperatures and the fuels must not interfere with flying operations by freezing and plugging filters. It has not been practical to make JP-5 from some petroleum crudes because the freezing point cannot be met along with the required flash point. Dimitroff et al (2) examined the influence of composition on freezing point of several types of fuels. They found the saturate fraction of a fuel usually exerted the greatest effect on freezing point but the aromatic fraction seemed to be important in some cases.

NRL has related the freezing point of JP-5 type fuels to the n-alkane content, specifically n-hexadecane (1). This relationship applies to jet fuels derived from alternate fossil fuel resources, such as shale oil, coal, and tar sands, as well as those derived from alternate fossil energy sources such as shale oil, coal, and tar sands. In general, jet fuels from shale oil have the highest and those from coal the lowest n-alkane content. The origin of these n-alkanes in the amounts observed, especially in shale derived fuels, is not readily explained on the basis of literature information. Studies of the processes, particularly the ones involving thermal stress, used to produce these fuels are needed to define how the n-alkanes form from larger molecules which are cyclic or branched. The information developed will significantly contribute to the selection of processes and refining techniques for future fuel production.

### PYROLYSIS MECHANISMS

A large n-alkane breaks apart by a free radical mechanism to yield smaller hydrocarbons, both n-alkanes and 1-olefins. This process, as originally diagnosed by Rise (3), ultimately yields mostly small olefins with 2 to 4 carbon atoms. This behavior is encouraged by high temperatures and low pressures. At conditions

more typical of shale retorting and delayed coking, however, Fabuss-Smith-Satterfield (4) behavior occurs. In this situation, a single fragmentation step occurs and equal amounts of n-alkanes and olefins form. Further, the yield is about the same for hydrocarbons in the intermediate carbon range. Unbranched olefins formed in the pyrolysis reactions readily convert to n-alkanes by hydrogenation.

Thus, formation of n-alkanes in the jet fuel distillation range can be explained if large n-alkanes are present in the crude oil source. Quantities of large n-alkanes are insufficient, however, to explain the amounts found - up to 37% n-alkanes in the jet fuel range (1). Other possible precursors to small straight chain molecules are substituted cyclic compounds. Attack in the side chain obviously affords a path to an n-alkane. Aromatic hydrocarbons, esters, acids, amines, and ethers also have the potential to form n-alkanes if an unbranched alkyl chain is present in the molecule.

#### EXPERIMENTAL STUDIES

Carbon-13 nmr studies indicate that oil shale rock contains many long unbranched straight chain hydrocarbon groups (5). The shale oil derived from the rock also gives indication of considerable straight chain material with large peaks at 14, 23, 30, and 32 ppm in the C-13 nmr spectrum.

Separation - A residue from Paraho shale oil was obtained by vacuum distillation at 40 torr to an end point of 300°. The residue was then separated on activated silicagel into a saturate fraction, an aromatic fraction, and a polar fraction. The saturate fraction was removed from the silica with n-pentane solvent, then the aromatic fraction was removed with a 25:75 benzene: n-pentane solvent. The polar fraction was desorbed with 25:75 benzene: methanol solvent. Although the polar fraction required methanol for desorption, it was only slightly soluble in methanol. It dissolved readily in benzene, however. The nitrogen content of various eluates was determined by Drushel's method (6) as an indication of the separation efficiency. The pentane eluant contained no nitrogen and the polar fraction (benzene:methanol) contained 97% of the recovered nitrogen. If 100% benzene was used to desorb the aromatic fraction, up to 20% of the nitrogen was found in the aromatic fraction. The nitrogen concentration in the separated fractions was 2.5% in the polar, 0.13% in the aromatic and less than 0.01 wt% in the saturate fraction. The input N concentration in the residue was 2.2 wt%.

The distillation residue comprises 48% of the shale crude oil. On a chemical basis, the polar compounds comprise 71%, the saturates 13% and the aromatics 16% of the recovered residue. Mass recovery from the separation was 85% but nitrogen recovery was much less, 70%. The material retained on the silicagel, consequently, appears to be highly polar and high in nitrogen.

Carbon-13 nmr Analysis - Samples of the various fractions were submitted to analysis by C-13 nmr. The C-13 spectrum affords a distinct separation of the aromatic and aliphatic absorption regions plus a good resolution of many peaks due to specific molecular structure. Thus, a good amount of useful information can be obtained even for a complex mixture such as a fuel fraction. With respect to

the present study, the aliphatic region of the spectrum is of particular importance.

Quantitative analysis of the aliphatic region was attained by including a known amount of methanol in the sample as an internal standard. A long unbranched fragment will exhibit peaks at several positions in the aliphatic region of the spectrum. The peak corresponding to the methyl end group ( $\alpha$ -carbon) appears at 14 ppm with reference to tetramethylsilane at zero ppm. The  $\text{CH}_2$  group adjacent to the methyl group ( $\beta$ -carbon) absorbs at 23 ppm and subsequent absorptions appear at 32 and 29.5 ppm for the  $\gamma$ - and  $\delta$ -carbons. Beyond this, all other  $\text{CH}_2$  groups in a long unbranched chain absorb at 30 ppm. Therefore, this latter peak would be quite large for a long chain. In fact, the ratio of the area of this peak to the  $\alpha$ -  $\beta$ - or  $\gamma$ -peak can afford information on the average chain length of the unbranched fragment.

A spectrum for the aliphatic region of the polar fraction from the shale residue is shown in Figure 1. The distinctive peaks at 14, 23, 32, and 30 ppm demonstrate the presence of significant amounts of long unbranched groups in this fuel fraction. The 29.5 peak appears as a shoulder on the 30 peak and these two peaks were integrated together. Quantitation of the spectral information using the methanol internal standard gives the data listed in Table I. As expected, the content of long unbranched alkyl groups is greatest for the saturate fractions. Further, the straight chain alkyl groups in the saturate fraction are longer on the average than those in the aromatic and polar fractions. We conclude that there is a definite potential for making n-alkanes and 1-olefins in the jet fuel distillation range by cracking compounds found in the heavier shale oil cuts.

Pyrolysis - The residue fractions have been stressed at conditions corresponding to the petroleum refining process known as delayed coking (7). These conditions are about 450°C and 90 psi pressure. Each thermal stress was conducted in a 1/4 inch o.d. 316 s.s. tube fitted with a stainless steel valve via a Swagelok connection. The tube, with a weighed amount of sample (approximately 0.1 g), was attached to a vacuum system, cooled to -78°C, and pumped to remove air. The tube was then thawed and the cooling/pumping process repeated. The tubes were heated by inserting them into 9/32 inch holes in a six inch diameter aluminum block fitted with a temperature controller.

At the close of the heating period, the tubes were cooled to -78°C and the valve removed. A mixed solvent of n-pentane and benzene (50:50) was added to the tube which was then capped and warmed to room temperature. The solution and a subsequent rinse were transferred to a screw cap vial which was then stored in a freezer until analysis. A weighed amount of toluene was added as an internal standard prior to analysis.

The stressed samples were analyzed by two techniques, both based on gas chromatography. In the first, the solution with internal standard was injected into a 10 ft, 1/8 inch o.d., 5% OV-101 column which was programmed to 260°C at 12°/min after a 5.0 min initial hold at 60°C. The JP-5 cut was integrated as a single sum and compared to

the internal standard to determine the yield of JP-5 from the pyrolysis experiment. The initial gc cut point for the JP-5 was set midway between *n*-octane and *n*-nonane and the final point midway between *n*-hexadecane and *n*-heptadecane. The gc baseline did not rise during this portion of the analysis, hence reliable integration was obtained.

The second gc technique determined the individual *n*-alkanes and 1-alkenes in the pyrolyzed sample. A 100 m wall coated glass capillary gave the required resolution and the *n*-alkanes and 1-alkenes stood out as distinct, well resolved peaks. OV-101 or OV-17 wall coatings provide adequate separation. A carrier gas flow of one cc/min was combined with an inlet split ratio of 50:1 and a 310°C injector temperature. The column temperature was raised to 250°C at 4°/min after an 8.0 min initial hold at 80°C. Peak identification was based on retention time matching with *n*-alkane and 1-alkene standards.

Pyrolysis of the saturate fraction for 30 min at 450°C gave the *n*-alkane and 1-alkene yields shown in Fig. 2. The *n*-alkanes predominate over the 1-alkenes at all carbon numbers for this sample. This was generally true for all fractions and all stress times. The 1-alkenes were less stable than the *n*-alkanes and the larger alkenes were very minor products for stress times 60 min and longer. Fig. 2 indicates that the product exhibits a plateau in the 10-14 carbon number range, an integral part of the JP-5 distillation range.

The effect of stress time on yield is illustrated in Fig. 3. The *n*-alkane + 1-alkene sum for each carbon number is plotted. For a 16 min stress the yield for carbon numbers 10 through 14 are almost identical. Consequently, one-step Fabuss-Smith-Satterfield pyrolysis (4) is controlling. The total yield increases at 30 min but the shift to a maxima at C-10 indicates product is forming and undergoing secondary decomposition. This trend is extended significantly at longer times such as shown by the 60 min data. Here the maximum is outside the JP-5 range and the yield of molecules with 16 or more carbons is quite low.

For the polar fraction, the combined *n*-alkane + 1-alkene yield increased up to 60 min stress time, then reversed (Fig. 4). The yield of the larger molecules - 15 carbons and above - was drastically reduced at 180 min. Even at 16 min the products obtained in largest yield were on the low end of the JP-5 distillation range. This is consistent with the lower value found by nmr for the average unbranched alkyl chain length. The aromatic yield pattern fell between that for the saturate and polar fractions.

A summary of the yield data for all fractions stressed for various times at 450°C is presented in Table II. The saturate fraction affords the highest yield of JP-5 but the other fractions give yields in excess of 20% at intermediate stress times. The polar fraction requires a longer stress time to attain its maximum yield of JP-5.

The potential *n*-alkane yields in the JP-5 cut are also listed in Table II. These values were obtained by summing the capillary gc yields of *n*-alkanes and 1-alkenes for carbon numbers 9 through 16. This total was divided by the JP-5 yield in the left portion of Table II to give the potential *n*-alkane yield. The saturate fraction

attained the highest potential *n*-alkane yield, 22.7% at 16 min stress. The aromatic and polar fractions also gave about 20% yields but these came with longer stresses. The potential *n*-alkane yields for all fractions fell off at longer stress times.

#### DISCUSSION AND CONCLUSIONS

The best yield of the JP-5 cut comes at different times for the various fractions, but a time in the 60 to 120 min range would appear to be the optimum time for good yield at 450°C. The longer time would be preferred with respect to lower potential *n*-alkane yield.

None of the fractions gave *n*-alkane yields approaching the 37% amount found in the Shale-I JP-5<sup>(1)</sup>. A temperature different than the 450°C used here might affect the conversion percentage. Further the combined saturate, aromatic, and polar fractions may interact under pyrolysis conditions to give higher potential *n*-alkane yields than the fractions stressed independently.

#### ACKNOWLEDGMENT

The authors thank Dr. Hyman Rosenwasser of the Naval Air Systems Command for funding support.

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TABLE I. Carbon-13 nmr Examination of  
Shale Oil Residual Fractions

<u>Fraction</u>	<u>Wt. % Carbon in</u> <u>Aliphatic Region</u>	<u>Wt. % Unbranched</u> <u>Alkyl Groups*</u>	<u>Average Chain</u> <u>Length**</u>
Saturate	100	40	43
Aromatic	60	21	14-22
Polar	56	30	20

\* Sum of areas of absorption peaks at 14, 23, 30, and 32 ppm.

\*\* For unbranched alkyl groups: based on ratio of 30 ppm peak area to average of 14, 23, and 32 peak areas.

Precision:  $\pm$  10%

TABLE II. Product Yield\*

<u>Pyrolysis</u> <u>Time (min)</u>	<u>JP-5 Yield</u>			<u>Potential n-alkane Yield</u>		
	<u>SAT.</u>	<u>AROM.</u>	<u>POLAR</u>	<u>SAT.</u>	<u>AROM.</u>	<u>POLAR</u>
16	20.4	18.8	5.7	22.7	14.4	14.7
30	28.0	24.4	11.9	20.8	19.4	20.8
60	27.3	-	20.0	15.5	-	21.3
120	-	12.0	22.5	-	15.1	12.8
180	-	-	16.3	-	-	15.5

\* Yield in %, potential n-alkane yield is for JP-5 cut; pyrolysis temperature - 450°C.

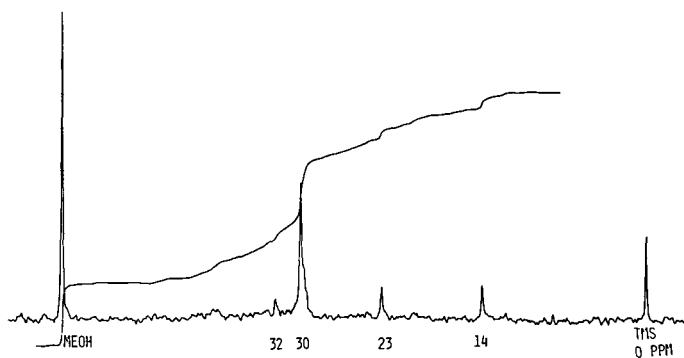


FIG. 1. C-13 NMR SPECTRUM OF SHALE OIL RESIDUA POLAR FRACTION, ALIPHATIC REGION, TMS REFERENCE, METHANOL INTERNAL STANDARD.

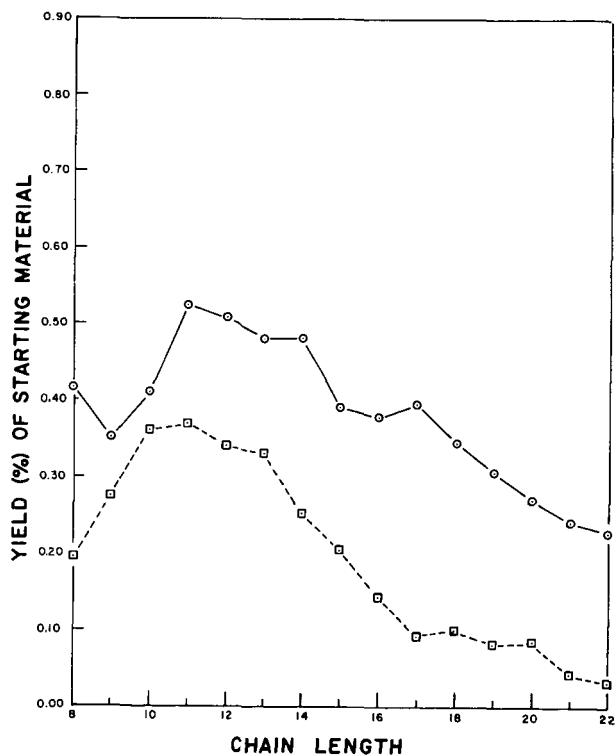


FIG. 2. PYROLYSIS OF SHALE RESIDUA SATURATE FRACTION AT 450°C FOR 30 MINUTES; UPPER CURVE -- N-ALKANES, LOWER CURVE -- 1-ALKENES.

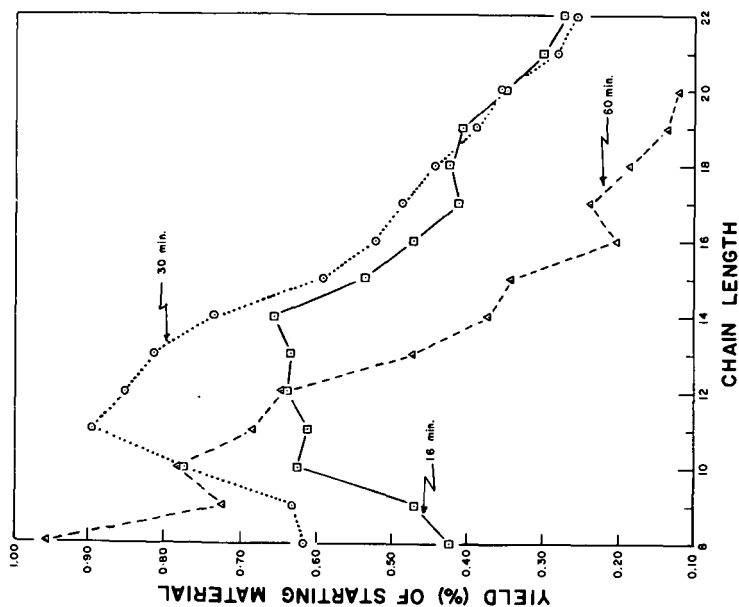


FIG. 3. PYROLYSIS OF SHALE RESIDUA SATURATE FRACTION AT 450°C; YIELD IS SUM OF N-ALKANE PLUS 1-ALKENE FOR INDICATED CHAIN LENGTH.

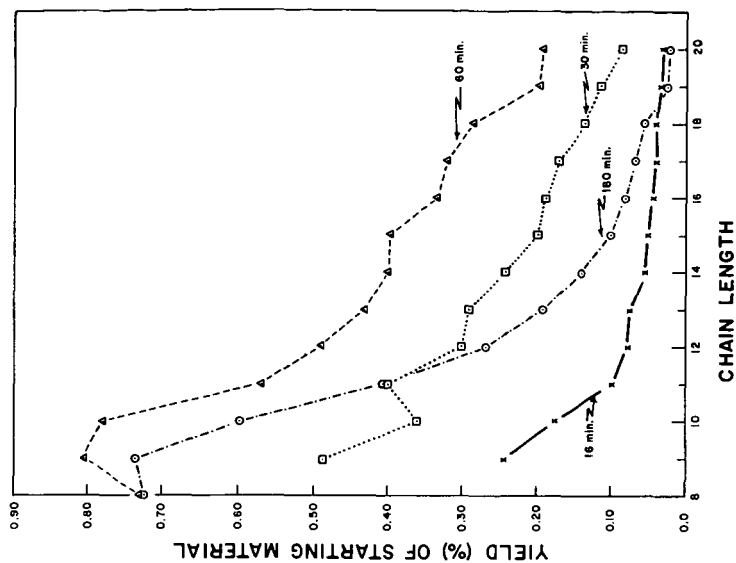


FIG. 4. PYROLYSIS OF SHALE RESIDUA POLAR FRACTION AT 450°C; YIELD IS SUM OF N-ALKANE PLUS 1-ALKENE FOR INDICATED CHAIN LENGTH.